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Diffusion in Solid Silicates: A Tool to Track Timescales of Processes Comes of Age

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Abstract

Understanding how processes occurring on a wide range of temporal and spatial scales combine to produce a stable dynamic Earth is a major goal of the Earth scientist. Determining durations of processes is a key step toward attaining that goal. Records of incomplete diffusive equilibration preserved in minerals are uniquely suited for the purpose of unraveling timescales of a variety of processes. Compositional zoning in minerals is like the tracks of a CD that can be decoded with suitable technology. This review discusses the causes for the limited use of this tool until recently and how these hindrances are being overcome. Examples are presented to illustrate that diffusion modeling can clock processes that last from only a few days to those that last over tens of millions of years, recorded in rocks that range in age from current volcanic eruptions to condensates from the early solar nebula.

INTRODUCTION

Prologue: A Historical Background

The study of diffusion in solids has arguably had the most checkered history among all aspects of study of condensed matter. It may well hold the record for the longest gap between the observation/application of a phenomenon and its explanation. Since the first metallic alloy was produced in the Bronze Age, the first piece of iron rusted in the Iron Age, and the first piece of clay was fired to produce pottery, humans have been dealing with, and manipulating, diffusion in the solid state. Yet chemistry, or reactivity, was considered to be the nearly exclusive domain of fluids (liquids and gas) and much of chemical theory was developed to handle these states of matter. Indeed, revolutionary progress in the understanding of matter in the late nineteenth and early twentieth century helped to underscore the difficulty of reaction in crystalline solids. X-ray diffraction revealed the close packed, ordered periodic structure of crystals with an energy landscape where atoms/ions sat (vibrated) in periodically arranged valleys separated by energy barriers. Statistical thermodynamics and Boltzmann distribution laws highlighted the unlikelihood of two particles occupying the same valley in the energy landscape, let alone occurring simultaneously on the slope or peak of an energy hillock. The impossibility of atomic encounters, or chemical reaction, could be quantified! Of course, this intellectual barrier did not hinder the production of even more complex alloys at the same time. Nor did it hinder the same tools of X-ray diffraction from discovering an increasing array of mineral solid solutions. Diffusion in the solid state had already been observed separately by W. Spring and Roberts-Austen in the nineteenth century, but the understanding of crystallography and thermodynamics only served to raise the barrier on the path to an explanation. Breakthroughs were ultimately achieved rapidly between 1925 and 1930 through the seminal works of Smekal, Frenkel, Schottky, and Jost. They developed and documented the concept of point defects in crystals. Jost (1937) notably summarized these early thoughts in his now classic monograph. In an interesting twist of the history of science, once point defects were conceptualized, the same laws of Boltzmann distribution were used to quickly demonstrate that it was impossible to have perfect crystals without point defects at any temperature above absolute zero—a defective crystal had higher entropy that helped to reduce its free energy and stabilize it with respect to a perfect, idealized crystal. Just as a car cannot move in a fully packed parking lot but a single vacant slot allows all the cars to be moved around, the existence of point defects ensures that diffusion will occur, however slowly, in all solid materials. There is a finite probability that a vibrating atom in a crystalline lattice would exchange places with a vacant site (one possible kind of point defect), whether or not a chemical gradient exists. Diffusion in the solid state is ubiquitous. Understanding transport in the solid state has ushered in the era of solid-state electronics that is enabling this text to be typed today. Once a transport mechanism was identified, the mathematical structure for describing the evolution of such a system was found already to be in place—the random walk formulae (in essence, $x^2 \sim Dt$) derived by Albert Einstein as a follow up to his doctoral thesis in 1905 and obtained practically simultaneously by M.v. Smoluchowski in 1906. These led to the same differential equations and solutions

that A. Fick had obtained about 50 years earlier in 1855 in his study of fluids and biological systems. The same macroscopic laws of diffusion were found to describe atomic motion in solid systems, even though the underlying mechanism of diffusion was completely different. We have just completed the centennial celebrations of the Einstein and Smoluchowski equations, simultaneously with the 150th anniversary of Fick's laws. It is sobering to recognize that an explanation of diffusion in solids, a process that has literally shaped our daily lives for millennia, came after such landmark and abstract scientific accomplishments as the theory of relativity, statistical mechanics, and quantum mechanics.

Diffusion and the Earth and Planetary Sciences

The ubiquity of diffusion in the solid state implies that its application in the Earth and planetary sciences is multifaceted. Diffusion in the solid state finds applications in the understanding of reaction mechanisms of minerals, deformation and flow of mantle materials or glacial ice, weathering and maintenance of historical monuments, and many other areas. It is not possible to do justice to all of these aspects in one review. Some aspects not covered here may be found in Watson & Baxter (2007) and Ganguly (2002); Chakraborty (1995) and Watson (1994) discuss diffusion in melts, Chakraborty (2005) provides a short introduction to diffusion in the Earth sciences for material scientists, and Boudreau (2000) reviews diffusive processes at low temperatures, e.g., during diagenesis. Here, I focus on one specific but broad and powerful application of diffusion in the solid state—its role in determining the duration of terrestrial and planetary processes. Duration, or timescale, of processes plays a central role in the understanding of dynamic systems such as the planet Earth and the Solar System. One of the fascinating aspects of the Earth sciences is to study how processes occurring on a spectrum of timescales are intertwined. The decay of radioactive isotopes has been the trusted timekeeper for most processes, mainly because the running of this clock is unaffected by environmental physicochemical variables. However, this aspect is also the most notable limitation of this method. To measure the duration of short processes, it is necessary to have clocks that run faster (i.e., decay faster for a radioactive system), as seen, for example, in the gears of a mechanical clockwork. But because radioactive clocks run inexorably, short-lived radiogenic isotopes are extinct in older rocks. Therefore, alternate tools for measuring ancient, short duration processes are necessary. This is one of the major areas where the solid-state diffusion clock can find application.

In the following, I commence with a general discussion of geological clocks and their characteristics. After discussing how the diffusion clock works and some of its strengths and weaknesses, I address the main reasons behind the graduation of diffusion modeling from a possible to a practical tool. I proceed to discuss the nature of diffusion in solid silicate systems, i.e., rocks, meteorites, and minerals, and how our understanding of diffusion mechanisms in these materials has improved and changed qualitatively from traditional textbook descriptions. This is followed by a discussion of some of the factors that control diffusion rates in solid systems. I conclude with some examples of applications to illustrate the breadth of the method,

the choice being guided by the intention of introducing a representative variety of modeling tools/methods that have been developed. In the process I outline why the term geospeedometry is somewhat of a misnomer.

MEASURING TIMESCALES: THE CHARACTERISTICS OF CLOCKS

Kinetics (time-dependent evolution) of some process is necessary to measure time. **Figure 1** is a generalized diagram that illustrates the evolution of any system, including radioactive decay, as a function of time. The curve describing the temporal evolution of any system is essentially made up of three branches—a short-time branch, where no perceptible (depending on the resolution of the measuring device) evolution occurs ($R \sim 0\%$ in **Figure 1**); an intermediate branch of interest, where the extent of change (e.g., diffusion, deformation, chemical reaction, ordering, radioactive decay) is a function of time [$R(t)$ in **Figure 1**] and can be used as a clock; and a long-time branch, where the evolution is complete ($R = 100\%$ in **Figure 1**), the system has effectively reached equilibrium, and is independent of time. The first and the third

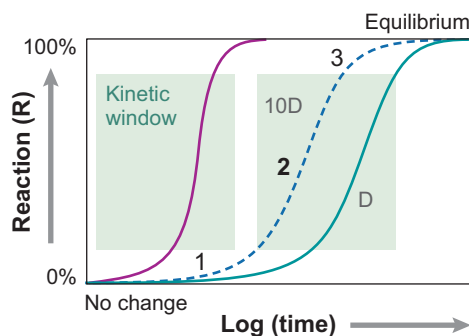


Figure 1

A generalized diagram to illustrate the evolution of systems (shown here as percent R) and their utility as clocks. (1) ($R \sim 0\%$), (2) $R(t)$, and (3) ($R = 100\%$). To clock any geological process, it is necessary to identify physicochemical processes (radioactive decay, diffusion, deformation, etc.) with characteristic timescales that coincides with stage 2 of the geological process of interest (the “kinetic window,” schematically shown here in *light green*). In addition, the incomplete transformation in stage 2 needs to be frozen in the rock record so that it may be retrieved quantitatively at a later time. Diffusion in solid silicates fulfills both these requirements. Also shown are (a) the effect of uncertainties in our knowledge of rates of transformation (diffusion coefficients, in our case). An error/uncertainty in this quantity of an order of magnitude (rate = D versus $10D$) translates to an error in the determined duration of a process of the same magnitude (for a given observed degree of transformation, R). This highlights the necessity of knowing kinetic rates accurately. (b) The versatility of diffusion processes. It is possible to find diffusion coefficients of some element in some mineral that lies in stage 2 of any geological process of interest. For a process that is too fast to be clocked (i.e., lies to the left of the kinetic window) by the diffusion of elements marked by the green lines (*solid or dashed*), it is possible to find a different diffusion process (*purple line*) whose kinetic window lies in the right region. Examples may be diffusion of different elements in a single mineral such as plagioclase (Li: fast, Mg: intermediate, NaSi-CaAl: slow).

branches are independent of time, and consequently of little interest as clocks. Some examples may clarify the concepts. Using a radioactive decay system, e.g., ^{87}Rb - ^{87}Sr , it is not possible to date objects/processes that are only a few decades or centuries old because on this timescale, no perceptible (resolvable with current instruments) decay of ^{87}Rb occurs. For many terrestrial processes, the decay system finds itself in the second branch, where the process is not complete and both daughter as well as mother isotopes are still available. This is the reason for the widespread utility of the Rb-Sr system as a dating tool. For an example of the third branch where the reaction is complete, consider an isotopic system with a faster decay constant, e.g., ^{26}Al - ^{26}Mg . This system, with a half-life of approximately 1.5 million years, is now extinct and is also useless today for dating objects/measuring the duration of short processes. Analogous situations for diffusion would be (a) short timescale, where no measurable diffusion of the species of interest occurs; (b) intermediate timescale, where measurable diffusion occurs, but the system is frozen without the diffusive process going to a conclusion (e.g., compositionally zoned crystals are available); and (c) diffusion is complete and equilibrium has been achieved (e.g., concentration gradients have been homogenized). Equilibrium by definition does not contain any information about time. This has been stated eloquently by S. J. Gould: “. . . for perfection covers the track of time.”

The Diffusion Clock

The connection between diffusive processes and timescales was established primarily through analytical solutions to the diffusion equation derived to determine the temperature at which crystals undergoing cooling cease to exchange atoms with their surroundings (the concept of closure temperature, with parallels in many fields of science, e.g., fictive temperature in glass sciences). The general approach that describes all of what follows relies on expressing diffusion coefficients as a function of time, $D(t)$, through its dependence on temperature, T . This is accomplished via an Arrhenius-type equation with activation energy, Q , i.e.,

$$D(t) = D_0 \exp\left(\frac{-Q}{RT(t)}\right).$$

This equation describes diffusion that occurs in any thermal event, i.e., along any temperature–time path, $T(t)$. Next, this time-dependent diffusion coefficient is used in the diffusion equation, stated in one-dimension as $\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D(t)\frac{\partial C}{\partial x}\right)$. The equation describes how concentration gradients (i.e., concentration profiles), (dC/dx) , evolve as a function of time. Given $D(t)$ and a measured concentration gradient, it is therefore possible to obtain information about time or the duration of the process. The solution of this equation yields the total amount of diffusion that occurs in a given thermal history,

$$\int_0^{t_f} D(t') dt',$$

where t_f is the total duration of the thermal process and t' is the time variable. The measured concentration profile is the integrated result that is obtained due to diffusion along the entire temperature-time path. Other essential inputs to the modeling are the initial profile shapes and the boundary conditions under which diffusion takes place—these are obtained from petrological analysis. The first analytical solutions to the equation were derived for systems undergoing cooling, and consequently, if the closure temperature were known independently, then the cooling rate could be determined from the same set of observations. The development of the closure temperature formulations stands on the solid foundation provided by a series of three classic papers by Dodson (1973, 1976, 1986). The idea of extracting cooling rates was developed by Lasaga et al. (1977) in a pioneering paper, followed up in more detail by Lasaga (1983). Here, he related the cooling rate obtained to rates of exhumation of metamorphic rocks and coined the term geospeedometry. However, only a few applications of diffusion modeling actually end up calculating rates of motion (e.g., exhumation/burial) and hence application of this term to the entire field of obtaining timescales from diffusion modeling is somewhat misplaced, particularly because it is duration rather than rates that is the primary information that is extracted. Subsequent significant improvements to the closure temperature formulation were made by Ganguly & Tirone (1999), who extended the formulation to be applicable to a wide class of systems where the memory of the initial condition is not entirely lost (as required in the Dodson formulations). Related developments are described in Giletti (1986), Eiler et al. (1992), and Jenkin et al. (1994), where diffusive exchange between multiple phases is considered with infinite diffusion rates in the intergranular medium; effects of finite transport rates in the intergranular medium were considered by Livi et al. (2002) and Dohmen & Chakraborty (2003). More generally, the time information extractable from diffusion modeling is the total duration of any thermal event rather than just the cooling rate—this has been discussed and pointed out by Chakraborty & Ganguly (1991) and Stüwe & Ehlers (1996). Lasaga & Jiang (1995) demonstrated how inverse modeling tools may be applied to diffusion modeling when some geological “common sense” is used to constrain the mathematical model. Finally, Chakraborty (2006) discusses the general approach to diffusion modeling (other than inverse modeling) along with advantages and pitfalls associated with various steps.

Utility and Limitations of the Diffusion Clock

Given the variety of kinetic processes that may affect minerals, it is worthwhile to consider why diffusion should be chosen for special treatment. Kinetic processes that affect solid materials include nucleation, crystal growth, dissolution/precipitation or other chemical reactions, reactions accompanied by fluid flow, phase transitions, order-disorder transitions, exsolution, and diffusion.

Of these, nucleation and crystal growth can occur by different mechanisms and, consequently, the first step of modeling these processes is to identify the law (i.e., the equation) they obey in a given case. Notwithstanding this difficulty, empirical equations combining nucleation and growth have been used to determine timescales.

Examples include crystal size distribution (CSD) analysis in igneous and metamorphic rocks [numerous studies following the initial studies by Cashman and coworkers: Cashman & Marsh (1988), Cashman & Ferry (1988)] and extensions of the Cahn-Avrami formulations (e.g., Rubie & Ross 1994). Dissolution, precipitation, or other forms of chemical reactions typically involve several of these processes, in addition to some diffusion, as a rule. Reactions with fluid flow require the additional treatment of fluid flow equations and often involve parameters (e.g., permeability) that are poorly constrained. The theory of phase transitions is highly developed, but the rates of most of these are too fast to be useful for measuring timescales of most geological processes (i.e., the time window of the process is too far to the left of the region of relevance in **Figure 1**). Order-disorder, exsolution, and diffusion are all different manifestations of the same kinetic process, and have all been used to measure timescales of geological and planetary processes. Although there are different ways to treat the kinetics of order-disorder, the formulations are well defined; for diffusion the process is always governed by a well-defined mathematical law—Fick's law of diffusion (see below for a detailed discussion).

Within this context, Chakraborty (2006) has discussed why diffusion is a powerful tool for determining durations or timescales:

- (a) It is a ubiquitous process. Natural minerals are typically solid solutions and so thermodynamics requires that the composition of the reactant and the product in an elementary step of any chemical transformation be different. Obtaining a product with a different chemical composition from that of the reactant requires diffusion of atoms to occur on some scale somewhere.
- (b) The process is governed by one well-defined, quantitative law. A combination of conventional petrographic skills to identify suitable initial and boundary conditions combined with modern numerical methods for solution of differential equations is necessary for usefully applying this law.
- (c) Under favorable circumstances, the durations/timescales are determined by modeling diffusion of the same elements that are also used to determine the pressure/temperature/dates of various events affecting the rocks. This allows the durations to be related to specific processes.
- (d) Radiogenic isotopes date events accurately, but it is by combining several such dates, with some consideration of closure of a system (typically dependent on consideration of diffusion), that one can conclude anything about durations or rates. Diffusion modeling yields durations directly.
- (e) Diffusion rates of different elements in the various minerals are spread over many orders of magnitudes at any given condition and so it is usually possible to find an element that fits the "window of opportunity" in **Figure 1** for any given process. In this connection, the rapidly increasing capability of measuring trace element and isotopic concentration gradients with increasing spatial resolution is of immense importance. This aspect is highlighted in **Figure 1** through the example of diffusion rates of different elements in one single mineral, plagioclase—timescales of a few days/weeks (e.g., Li) to the entire history of Earth (billions of years, NaSi–CaAl exchange) may be accessed at magmatic temperatures.

SIMS: secondary ion mass spectrometry

Nanosims: nanoscale secondary ion mass spectrometry

TOF-SIMS: time of flight–secondary ion mass spectrometry

RBS: Rutherford backscattering spectroscopy

NRA: nuclear reaction analysis

AFM: atomic force microscope

ATEM: analytical transmission electron microscopy

EBSD: electron backscatter diffraction

TEM: transmission electron microscopy

- (f) The temporal resolution of the tool is independent of age. This is by far the most important aspect of diffusion modeling, and one that demands that diffusion modeling be a part of the standard geochemical and cosmochemical toolbox. There is no other tool that is available to resolve and study processes that occur on timescales of a few weeks, decades, centuries, or even millennia a few billion years ago. Isotopes that decay fast enough to clock such processes would be extinct today.
- (g) The increased speed and resolution of analytical equipment means that it is possible to measure multiple compositional profiles/maps from the same sample. This affords the possibility of numerous cross checks—between information obtained from the diffusion modeling of the same elements in different grains (including the use of effects resulting from anisotropy of diffusion), different elements in the same mineral, and different elements in different minerals. This ability to obtain multiple measurements allows statistics to outweigh uncertainties that stem from lack of knowledge of initial or boundary conditions during diffusion. Examples of such applications are discussed below. The same procedure helps to identify compositional gradients that have been produced by processes other than diffusion.

Having outlined the merits of diffusion modeling, let us consider why this potentially valuable tool has not found wider application so far and how this is changing now. There are four main reasons for this. Silicates and oxides of interest to Earth and planetary scientists are among some of the most refractory materials known [e.g., zircon (Cherniak et al. 1997a,b; 2001; 2003)], and, consequently, diffusion rates in these materials are some of the slowest known. Measuring such slow rates within reasonable laboratory time frames was a major experimental challenge. Recent advances whereby the systems can be miniaturized to submicron and nanoscales have made these rates accessible. A simple consideration of the relation $x^2 \sim Dt$ indicates that for a given small value of D (e.g., $10^{-21} \text{ m}^2 \text{ s}^{-1}$) to be measured in a reasonable laboratory timescale, t , it is necessary to induce and measure spatial features (typically concentration gradients) on a correspondingly small scale. If the profiles are to be measured using an electron microprobe, then experiments would have to last 200 days to produce a measurable profile on the order of 10 microns. Using the nanoscale techniques available now, it is possible to do the experiment in 2 h. Similarly, if concentration profiles on the order of tens of microns produced over millions of years in nature are of interest to us, concentration profiles at the same conditions can be generated in the laboratory on a nanometer scale in a few days to weeks, eliminating the need for extrapolation. These have been made feasible by our ability to produce nanoscale concentration gradients (e.g., by deposition of thin films by laser deposition) and the ability to quantify these concentration gradients on submicron scales (e.g., using analytical tools such as SIMS, Nanosims, TOF-SIMS, RBS, NRA, AFM, ATEM, and white-light interference microscopy). Structural characterization on these spatial scales is possible using tools such as EBSD, TEM, and SEM; some examples may be found in Dohmen et al. (2002a), Dohmen et al. (2007), Milke et al. (2007), and Dohmen (2007). These advances are complemented by improvements

in the ability to achieve and control high pressures and temperatures. In particular, the combination of the thin-film approaches with high pressures and temperatures is proving to be a powerful tool to study, for example, the effect of water on rheology of mantle minerals (Costa & Chakraborty 2007).

The second aspect is the complexity of the diffusion process. Although simple models of diffusion on a periodic lattice are now well established, natural minerals are chemically and structurally complex—indeed, they are the most complex inorganic materials known. In addition, the Earth scientist is interested in rates of diffusion in these materials under extreme physico-chemical conditions, e.g., high pressures, and across multiple phase transitions and reaction boundaries. But with increased availability of data, theoretical analyses that consider the nature of diffusive coupling, mechanisms of diffusion based on analysis of point defect systematics, *ab initio* simulations, and diffusion in multiphase systems are all developing rapidly. An area that requires much further work is that of reactive diffusion, where diffusion and chemical reaction processes in solids occur simultaneously.

The third aspect is the quality of observation of the natural rocks and minerals. Inferring suitable initial and boundary conditions with which diffusion can be adequately modeled requires a level of precision of observation that is only recently becoming accessible through advanced imaging capabilities (e.g., EBSD for determining structural orientations). Quantification of element distribution maps, textures, grain boundary (and subgrain boundary) networks, etc., at increasingly higher resolutions and for increasingly larger number of elements (e.g., a variety of trace elements) is helping to identify suitable candidates for diffusion modeling and avoid pitfalls. Sophisticated tools of free energy minimization to constrain the pressure-temperature evolution of rocks are defining the conditions at which diffusion is to be modeled. The same tools should allow the important constraint of mass balance to be imposed to further refine the available diffusion models (e.g., differentiate between open versus closed system behavior in nature).

Finally, advances in computer speed and access have brought numerical modeling with realistic boundary and initial conditions within the reach of all scientists. Analytical solutions requiring demanding mathematics are mostly of use for testing these numerical tools or for developing generalized models.

Diffusion in Solids

There are many ways of defining diffusion, ranging from the purely mathematical, through atomistic (involving random jumps of atoms), to phenomenological macroscopic. The definition that I find to be completely general, and one that provides much physical insight without making any assumptions about mechanisms whatsoever, is that from Onsager (1945): the motion of one particle relative to the motion of other particles in a defined region of many particles.

There are two characteristics of diffusion that are worth noting. First, it is a very inefficient means of motion in the long term (**Figure 2a**), although in the short-term limit (**Figure 2b**) diffusion is very efficient. On the short timescale limit, a single jump from one node to the next is in fact considered to be instantaneous. The long-term

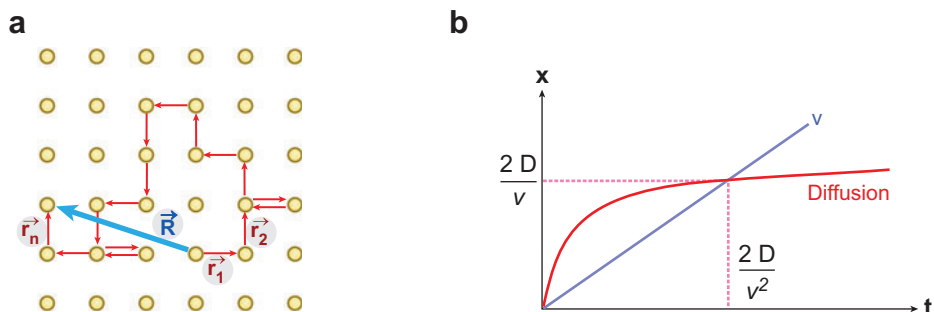


Figure 2

The nature of diffusion and its efficiency. (a) This picture of random walk on a uniform lattice shows how the net displacement after n -steps (blue arrow) is much less than n times the length of each jump (short red arrows). The nodes in the figure may be considered to be the lattice points where the atoms/ions sit/vibrate for long times, to jump intermittently to neighboring lattice points. This depiction highlights that diffusion occurs whether there is a concentration gradient or not. (b) It follows that on a short timescale, diffusion is as efficient as motion with a uniform velocity, v . In fact, if the jumps are considered to be instantaneous, then it can even be more efficient. It is only with increasing time that diffusion becomes inefficient. In that regard, it resembles motion with friction. How the time scales of diffusion and motion with uniform velocity scale with time are also shown, along with the crossover point. Adapted from Lasaga (1997).

behavior of diffusion, however, is often treated as motion with friction; it is easy to see why through **Figure 2b**. The second important characteristic that becomes apparent immediately from this discussion is that equalization of concentration gradients is not the cause, but a consequence, of diffusion. Diffusion occurs whether there is a concentration gradient or not.

A mathematical analysis of this random walk process leads to the well-known formula for a Gaussian distribution of concentration resulting from diffusion: $c(x,t) = A \cdot \exp(-x^2/\alpha Dt)$, where $c(x,t)$ is concentration as a function of distance/spatial coordinate (x) and time (t), D is the diffusion coefficient, A is a constant, and α is related to the dimension of the space in which diffusion occurs ($\alpha = 2n$ for diffusion in n -dimensions, e.g., $\alpha = 6$ for three dimensions). Practically all concentration distributions that result owing to diffusion from various complicated initial and boundary conditions are some function of this quantity. Most notably, for diffusion in the presence of an additional driving force F , the shape of the concentration distribution does not change—the driving force merely serves to “drift” the concentration distribution by a constant velocity, v , as shown in **Figure 3**. This is an important consideration when trying to decide whether a given concentration profile resulted from diffusion.

I have already discussed the important role of point defects in making diffusion possible in solids. **Figure 4** illustrates how this results in a fundamentally different nature of diffusion in solids from that in liquids or gases. First, if point defects occur rarely (as practically required by definition!) in a crystal lattice, then the exchange of position between a point defect and an atom has to be a rare event, i.e., diffusion

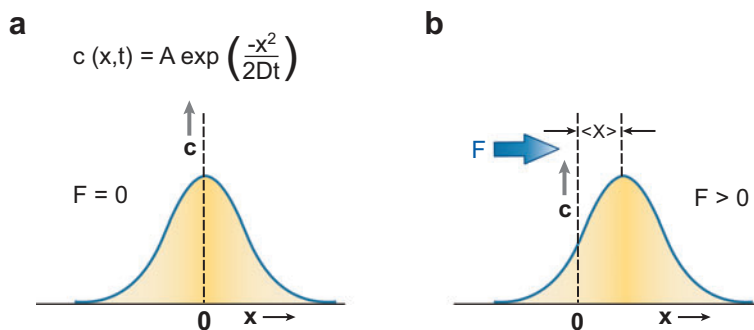


Figure 3

The nature of the solution to the diffusion equation, described by a Gaussian function: $c(x,t) = A \exp(-x^2/2Dt)$. Initially, all matter is taken to be concentrated at $x = 0$ (point source), from which it spreads out in both directions with time. Note that in the presence of a driving force, F , the shape of the profile remains unaltered—it is only translated, or drifted, laterally. This is an important criterion for recognizing concentration distributions produced by diffusion.

in solids is slow in general. Indeed, diffusion rates are directly proportional to the ease with which point defects can be produced in a solid. This is the basis of the frequently found scaling of diffusion rates to melting temperatures (the so-called concept of homologous temperature) because it is easier to produce defects in crystals at higher temperatures. Second, an atom can only diffuse when there is a point defect adjacent to it, whereas a point defect can always diffuse—it is surrounded by

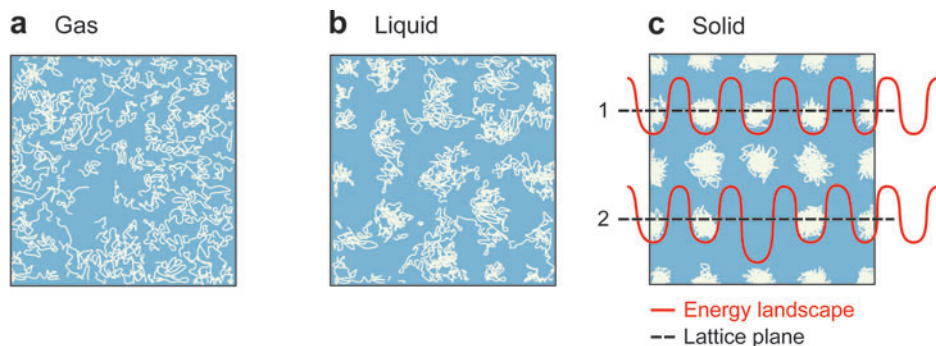


Figure 4

The distinction in nature of diffusion between solids, liquids, and gases. In liquids and gases, diffusing particles undergo random translational motion. In solids, they spend most of the time vibrating about periodically arranged lattice points of a crystal. Rare translational jump events interrupt the vibrational motion to cause diffusion. The energy landscape (*red line*) along one such lattice plane is shown along the dotted black line 1. In a similar line along 2, it is highlighted that a missing particle (vacancy) causes a local deepening of the energy well, making diffusion possible. It is clear that a vacant site can always exchange places with a particle and diffuse, whereas a particle has to wait a long time before it finds itself adjacent to a wandering, rare vacant site. Idea of illustration adapted from Kirkaldy & Young (1987).

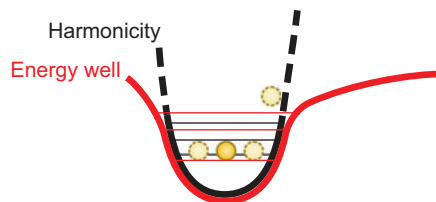


Figure 5

Illustration (exaggerated) of how the shape of the upper levels of the energy well (*red line*), and in particular the deviation from harmonicity (*black dotted line*), determine the course of diffusion in a solid. The yellow ball denotes the position of an atom, and the lighter yellow circles indicate positions it may occupy during vibration or a diffusive flight. One such light yellow circle illustrates how its position may be considered ready for a jump if the red potential is used, but it is still well enclosed within the black potential well. This aspect, related to proper description of electronic structure and bonding of a material, is crucial for the construction of realistic computer models of atomistic diffusion in minerals.

multiple atoms at any given time. This means that the net displacement of a point defect after any given time is much larger than the net displacement of an atom. This is a somewhat counterintuitive result because the one-to-one exchange of atoms for defects suggests that the two should move at the same “rates.” However, it is the flux of the two that needs to be balanced, and for $J_A = J_d$, and recognizing that flux = concentration \times velocity, one obtains $C_A v_A = C_d v_d$, where A represents atom; d, defects; J, flux; C, concentration; and v, velocity. Therefore, if the concentration of defects is on the order of parts per million, then the velocity (related to diffusion) of defects is approximately a million times greater than the velocity of the atoms. This is a very important consideration in deciding how long it takes to “equilibrate” the defects in a crystal—they can equilibrate much faster than concentration gradients.

A final aspect of diffusive jumps may be recognized by considering **Figure 5**. The probability of an atom escaping the potential well in which it sits is dependent on the depth of the well (or, alternately, the height of the energy barrier). But details of the transition probability depend on the shape of the potential well near its top, i.e., where anharmonicity and bonding effects of valence electrons of solids play an important role. This consideration is important for carrying out realistic computer simulations of diffusion in solids. Simplified computer models with harmonic potentials often fail to capture the essentials of the diffusion process. This is one of the major challenges for studying Fe-bearing silicates. The complex outer orbitals and high number of electrons (compared with, say, Mg, Si, and O) of Fe make it a challenge to carry out ab initio calculations with these, although modern methods are very close to cracking this problem. For example, Cococcioni et al. (2003) could carry out a simulation of fayalite that reproduced the structure faithfully, although they still had problems in describing the transport properties (their calculated fayalites were metallic rather than insulators!). Higher cut-off limits in more numerically intensive simulations that describe the electronic structure more faithfully would enable us to simulate transport processes in Fe-bearing silicates better.

All of the processes discussed above may be studied using computer simulations or detected using in situ spectroscopic methods (in particular, various nuclear spectroscopic methods, e.g., NMR or Mössbauer spectroscopy). However, the most well-known manifestation of these ubiquitous atomic jumps is in the homogenization of concentration gradients. Therefore, following up on this discussion of the nature of diffusion in solids, let us look at the phenomenological, macroscopic equation (Fick's law) that governs the concentration evolution owing to diffusion.

The law is stated as

$$J = -D\nabla C, \quad (1a)$$

or, in one dimension,

$$J = -D \frac{\partial C}{\partial x}, \quad (1b)$$

where J is the flux, D the diffusion coefficient, and C the concentration. The most straightforward implication of this statement is that the flux is proportional to the concentration gradient; the constant of proportionality is defined as the diffusion coefficient. However, in detail there are a number of subtleties that a user needs to be aware of for proper application of the law, and these have been discussed in the context of diffusion in silicate melts by Chakraborty (1995)—the first part of that discussion holds equally for diffusion in solids. The main points to note are (*a*) the statement of Fick's law would seem to suggest that diffusion occurs only when there is a concentration gradient. The subtly different fact is that diffusion occurs always; one has a net flux only when there is a concentration gradient. Therefore, in the presence of measurable concentration gradients, it is much easier to observe the process of diffusion. (*b*) The law is not steady state; it is local in space and time (**Figure 6**). (*c*) Flux depends on the diffusion coefficient as well as the concentration gradient. Therefore, a lack of observed diffusion (i.e., flux) may result either from slow diffusion rates or absence of concentration gradients. At the other extreme, very large concentration gradients always result in some diffusive flux, irrespective of how small the diffusion coefficient is. Presence of sharp concentration gradients, therefore, may be taken to indicate absence of diffusion; and if diffusion coefficients are known, then constraints (permissible upper limits) on the duration of processes may be obtained. Trepmann et al. 2004 used this approach to study timescales of metamorphism of some plutonic rocks from the Alps. This is also why it is difficult to produce diffusion barriers. (*d*) Different choices of reference frames (e.g., volume fixed, lattice fixed, laboratory), units for flux and concentration, and entities to describe chemical composition (i.e., chemical components) are possible. The same physical process yields different fluxes for different choices and it is important to be consistent. In particular, the choice of units should be made so as to ensure that the dimensions of diffusion coefficient are always $[L^2][T^{-1}]$. In a self-consistent framework, a diffusion process described using one formalism (reference frame, choice of units, choice of components) can always be converted to any other choice.

To end this section, I point out that Fick's law of diffusion is not valid on very short-length scales. One can easily convince oneself that at the limiting short-length scale situation of an infinite concentration gradient, using Fick's law yields the unrealistic

NMR: nuclear magnetic resonance

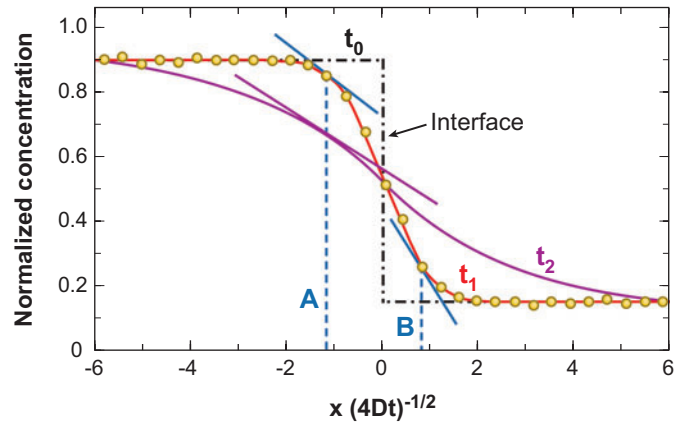


Figure 6

Illustration of the local nature of Fick's law of diffusion. Concentration profiles as a function of time in a diffusion couple where diffusion is governed by a constant diffusion coefficient, D . Dashed black lines indicate the initial concentration distribution and the location of the interface. Yellow circles show what measured concentrations may look like after time t_1 . The concentration gradient at a given point A (i.e., local in space), and therefore the diffusive flux in this system, changes as a function of time (slope = blue line at t_1 , purple line at t_2). At any given point of time t_1 , the concentration gradient at two different points A and B, and hence the diffusive fluxes at these points, are different (shown by the two blue lines). But at each of these points in space and time, Fick's law is valid locally. This figure also demonstrates why diffusion becomes progressively slower as equilibrium (i.e., no concentration gradient) is approached, and equilibrium is only approached asymptotically at infinite time.

result that flux is infinite. The multicomponent extension of Fick's law and its connections to chemical potential have been discussed in the review by Chakraborty (1995). And finally, anomalous or non-Fickian diffusion has not yet been documented in any geological material. The only well-known example of diffusion of water in glass/melt is a case of apparent non-Fickian diffusion because the process is one of Fickian diffusion coupled with homogeneous reaction (Wasserburg 1988, Zhang et al. 1991).

SPECIFICS OF DIFFUSION IN NONMETALLIC AND POLYPHASE SYSTEMS

Diffusion Mechanisms in Single Crystals

The description of diffusion we have provided above is valid for any solid (crystalline), continuous medium. For applications in the Earth and planetary sciences, it is important to consider some of the specifics of diffusion in nonmetallic systems, such as silicates and oxides, and the role of discontinuities, such as grain boundaries and surfaces, in a polycrystalline matrix. A fundamental distinction between diffusion in metals and nonmetals arises owing to the nature of bonding in these materials. Consider the process of creation of a vacancy, as illustrated in **Figure 7**. In a metallic material,

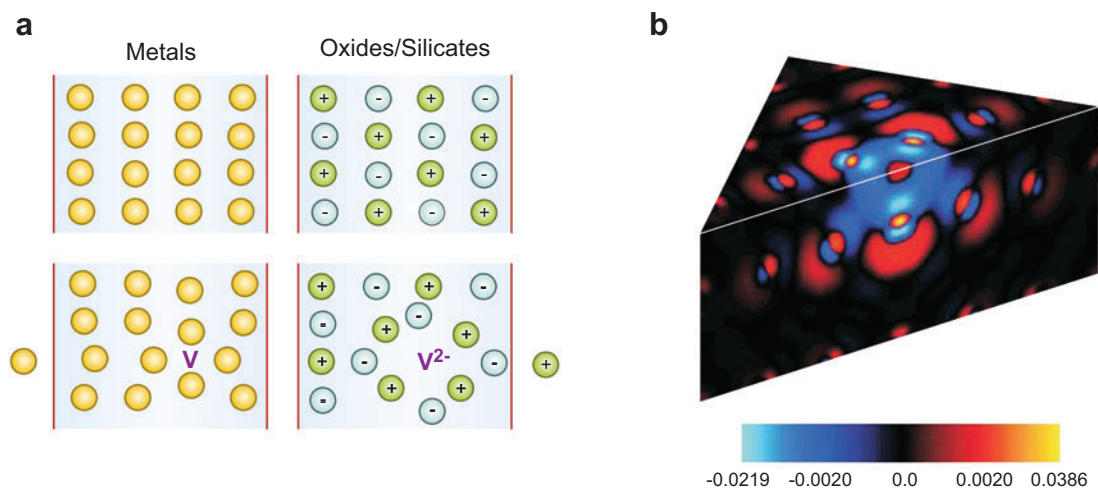


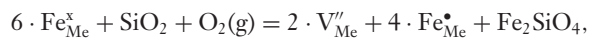
Figure 7

(a) Qualitatively different nature of point defects in silicates/oxides versus metals. A missing atom in a metal causes collapse of surrounding atoms into the vacant site. A missing ion (say, a cation) in a silicate/oxide structure produces repulsive forces between similarly charged ions (anions in this case) that now face each other, and neighboring cations are attracted to this site of missing positive charge. The overall effect is one of considerable polarization and distortion of the local structure, with energetic consequences for the process of diffusion. Potentials in such a region cannot be obtained by optimization of bulk properties, and electronic disorder needs to be considered explicitly. (b) Demonstration that such calculations are now becoming possible. Illustrated here is the visualization of electron density around a vacant Mg site in MgO (from Karki & Khanduja 2006).

creation of a vacancy can be modeled by plucking an atom out of the structure and removing it either to infinity or adding it on to the surface of the material. Computer simulations following this procedure yield quantitatively correct results. The same procedure cannot be carried out in this simplified form in an oxide or a silicate, where an ion has to be removed, and, therefore, charge balance has to be ensured. This added requirement immediately leads to various possibilities (e.g., simultaneous removal of a cation or an anion; compensation of the cation by charges elsewhere in the structure, for example, by the oxidation of a transition metal cation; and so forth). Once removed, the resulting vacancy is not merely a hole in the structure into which the surrounding atoms collapse a little. It is far more importantly a site of missing charge, which triggers polarization and repulsive forces operating between similarly charged particles now facing each other (e.g., anions, when a central cation has been removed). This results in considerable distortion and increase in local entropy at this site, which profoundly affects the energetics of point defect formation, migration, and all related diffusive processes. A brief discussion on this may be found in Chakraborty (1997), and computation of this effect in a material of geoscientific interest, MgO, may be seen in Karki & Khanduja (2006). This highlights the need for addressing electronic structures adequately in computer simulations, as we have observed already; we see below how

macroscopic measurements help to constrain the properties as well. Two very significant points should be noted from this simple illustration for applications in the Earth sciences. Empirical relationships developed for calculating quantities such as activation volumes in metals, based on simple volume-size-strain considerations resulting from a missing atom, are unlikely to be of much use for silicates and oxides because the consequence of placing a vacancy in a crystal of these materials is almost exactly the opposite. A second point is that the strong local distortion of charge distribution owing to the presence of a vacancy (or an interstitial, or an atom with a different charge) leads to very strong polarization effects and the energetics of this local site are completely different from those that may be obtained by optimization of bulk properties.

Point defects, by virtue of their very nature, occupy a position (a point) and have a certain energy associated with them—in other words, they have the essential characteristics of particles that make up crystals such as atoms or ions. These can be treated by the method of ensembles of statistical mechanics to define thermodynamic variables such as Gibbs free energy and chemical potentials and are amenable to treatment by the exact same thermodynamic formulations that are used for the study of electrolytes. In what follows, we deal almost exclusively with vacancies because diffusion mediated by vacancies is by far the most commonly encountered type. But it is implicit that other defects, such as interstitials, can be handled exactly analogously. The geo-material in which point defects have been studied in the greatest detail is olivine, and, consequently, olivine has become somewhat of a *Drosophila* of defect and diffusion studies. Recently, Dohmen & Chakraborty (2007) have reviewed and extended the analysis of point defects in this material. As shown by Nakamura & Schmalzried (1983) in a classic work, the formation of point defects in a typical ferromagnesian olivine is described by a (quasi) chemical reaction such as



where the Kröger-Vink notation has been used to state that an Fe^{2+} in the metal site can combine with some externally derived SiO_2 and O_2 to form vacant metal sites in a fayalite crystal, plus Fe^{3+} in other metal sites and an extra molecule of Fe_2SiO_4 . The Fe^{3+} charge compensates the missing charges in the vacant site. Obviously, this is far more than merely plucking an Fe atom out of an olivine crystal, such equations need to be formulated obeying three constraints: (a) mass balance: 6 Fe, 1 Si, and 4 O atoms on each side of the reaction; (b) charge balance: both sides of the equation are neutral overall; and (c) site balance: there are 6 octahedral metal sites on each side. Standard thermodynamic procedure can then be used to calculate the dependence of vacancy concentrations as a function of pressure, temperature, composition, and other intensive variables [see Dohmen & Chakraborty (2007) for a detailed example, including an explanation of the Kröger-Vink notation]. The point defect concentrations are related to diffusion rates. The simplest expression is of the form $D_{\text{Mg}}^* = f_{\text{Mg}} \cdot X_{\text{V}}^{\text{Mg}} \cdot D_{\text{V}}^*$, where D_{Mg}^* is the self-diffusion coefficient of Mg in olivine of a given composition, X_{V}^{Mg} is the concentration of Mg vacancies in the olivine (calculated from applying thermodynamics on the quasi-chemical equations of the

kind shown above), and D_V^* is the diffusion rate of the vacancy. f_{Mg} is the correlation factor, which accounts for the fact that all jumps are not completely random.

Once this structure is in place, it becomes clear that diffusion in a solid such as Fe-bearing silicate or oxide cannot be handled using the standard formalism of intrinsic and extrinsic diffusion mechanisms that are used for simple materials such as metals and salts. Intrinsic diffusion occurs when diffusion is mediated by thermally activated vacancies (or other point defects). This regime is characterized by a high activation energy (constituted of the sum of a defect formation energy and a defect migration energy) of diffusion and dependence of diffusion coefficients on pressure and temperature only, i.e., not on any chemical potential. This dominates in crystals of high purity and at high temperatures. Extrinsic diffusion (pure extrinsic, or PED) in contrast, is the situation where the activation energies are relatively low (constituted of only the migration energy) and diffusion coefficients depend, in addition to pressure and temperature, also on one or more chemical potentials. This dominates at lower temperatures. In Fe-bearing silicates, one has a situation that has features of both. Here the activation energy is a sum of a formation and a migration energy, but at the same time the diffusion rates are a function of at least one chemical potential, f_{O_2} (note that f_{O_2} is simply an alternate expression for measuring escaping tendency, analogous to chemical potential). The formation energy in this case is the energy change of a quasi-chemical reaction such as the one noted above, and is of much lower magnitude (approximately tens of kilo-Joules per mole, positive or negative) as a rule than the intrinsic defect formation energies (approximately several hundreds of kilo-Joules per mole, always positive). This regime, termed TaMED (transition metal extrinsic diffusion) by Chakraborty (1997), dominates at intermediate temperatures (**Figure 8**) for many situations of geological interest (e.g., above 800°C in olivines for Fe-Mg diffusion). Dohmen et al. (2007) and Dohmen & Chakraborty (2007) provide a detailed discussion, calculation, and experimental demonstration of diffusion by TaMED and PED mechanisms in olivine. Intrinsic diffusion is unlikely to be of much significance in impure natural minerals. A complete understanding of point defect mechanisms and how they control diffusion rates even in impure natural crystals allows diffusion coefficients at various conditions to be calculated and compared with experimental measurements. This ensures that errors from erratic measurements of diffusion coefficients or extrapolations do not mar diffusion modeling to extract timescales.

There are other examples of where point defect-based analysis is helping us to better understand and predict diffusion processes. For example, diffusion of monovalent ions, e.g., H^+ in olivine, occurs by two different mechanisms (Kohlstedt & Mackwell 1998) at very different rates and not considering these can cause large errors in estimates of timescales. In this, as well as in multicomponent systems such as garnets, the coupling of a given defect to diffusion of different species plays an important role and needs to be considered. The analysis of diffusion in the perovskite structure ($LaGaO_3$, which is doped to yield $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-(x+y)/2}$) by De Souza & Martin (2004) showed that in this oxygen vacancy-dominated material, diffusion of cations occurs via undissociated defect clusters so that activation energies of diffusion of different cations that occupy different sites are very similar. Aside from possible applications

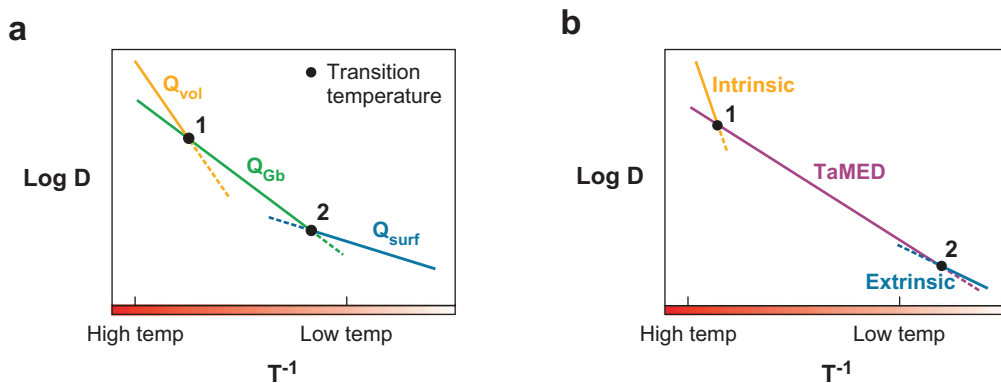


Figure 8

Illustration of how processes with high activation energy become more efficient at higher temperatures. The slope of lines on these log D versus $1/T$ plots are directly proportional to activation energy, Q , for a given process. (a) Somewhat counterintuitively, volume diffusion is actually more efficient at higher temperatures and in coarse-grained material (e.g., the mantle is a likely place for this in nature). However, surface diffusion dominates at lower temperatures characteristic of near surface processes. Grain boundary diffusion dominates at intermediate temperatures. The transition temperatures (1 and 2) shift depending on factors such as grain size of the material and whether the grain boundaries are wet or dry. (b) Exact parallels may be seen in the change of diffusion mechanisms within a single crystal. Only at the highest temperatures approaching the melting point is intrinsic diffusion expected to operate in materials such as silicates and oxides, high levels of purity are required in addition. In transition metal-bearing materials, the TaMED mechanism of diffusion (where diffusion depends on oxygen fugacity) is expected to dominate over a large temperature range. At low temperatures, pure extrinsic diffusion (PED) that is governed by only slightly different activation energy is the mechanism of diffusion. The transition temperatures (1 and 2) shift here as well depending on concentrations of various relevant trace elements. An added complication here is that the slope in the PED domain may be higher/lower than that in the TaMED domain (see text for details). Note however, that the uncertainty in extrapolation of diffusion coefficients is considerably more reduced than if one were to encounter the intrinsic-extrinsic transition (point 1).

in the Earth sciences, this has important implications for the longevity of solid oxide fuel cells.

A final example relates to SrTiO_3 —another material in the perovskite structure that is of interest in the optical industry. Gömann et al. (2005) found once again that Sr, Ti, and La all diffuse at about the same rates because they all make use of vacancies in the same sites to diffuse. This is an important consideration for understanding the diffusion behavior of trace elements in general. For example, Petry et al. (2004) found that the diffusion rates of trace elements Ni and Mn, as well as Fe-Mg, in ferromagnesian olivine are very similar for exactly the same reasons. This implies that one cannot expect compensation laws (proportionality between logarithm of the pre-exponential factor, D_0 , and activation energy, Q , in an Arrhenius-type equation), particularly those relying on ionic size, to be valid a priori. However, this connection between diffusion coefficients through point defects is at least as useful as a predictive tool for cases where no diffusion data are available. Gömann et al. (2005) found further

that the diffusion rate of an element such as Sr changed depending on how the Sr was introduced to the crystal. For example, when the Sr is physically implanted, the rates are slower—because the process effectively reduces the concentration of vacant Sr sites created by doping with La.

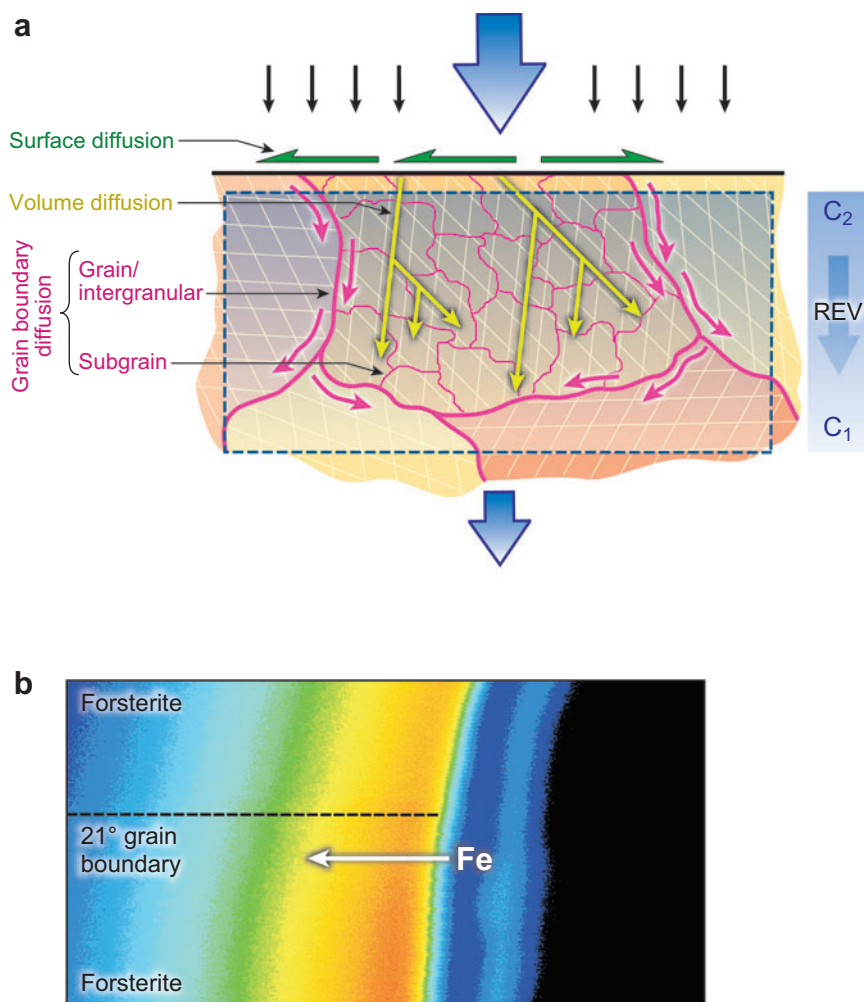
Diffusion in Grain Boundaries and Through Higher Dimensional Defects

One of the significant advances in studies of diffusion of solid systems has been the recognition that diffusion through discontinuities in crystal lattices (e.g., grain boundaries, surfaces) can be described using the same formalism as diffusion through the lattice structure. Indeed, modern materials science research invokes the concepts of point defects even for grain boundaries and surfaces (e.g., see Schmalzried 1995, Phillips 2001, Maier 2005). Therefore, to describe diffusion in a system containing several such boundaries (i.e., a rock, or a mineral with subgrain boundaries), the concept of a representative elemental volume (REV) that is well established in transport theory can be used. In essence, to reduce a system with discontinuities to a mathematically more easily tractable continuum, one chooses a volume in which all elements of interest are adequately represented. The system can be considered to be an endless repetition of such volumes. The approach should be familiar from the concept of unit cells in crystallography. Next, one finds a suitable scheme of averaging the properties of the individual parts and assigns this average value to the entire volume (which is subsequently depicted as a point in most applications). For diffusion in a polycrystalline material, these parts, as well as the principle of averaging, are illustrated in **Figure 9a**. Note that several paths may be found on all scales—these may be grain boundaries, crystal lattice, and intergranular boundaries in a rock; or diffusion along subgrain boundaries, dislocations, stacking faults, and linear/planar defect-free crystal lattice in a single crystal. Although some work has been carried out for characterizing such multipath or multidomain diffusion (e.g., Lovera et al. 1989, Lee 1995), this remains an area for much future research. However, handling diffusion in such polycrystalline materials is not inherently difficult, as long as these boundaries are all static. Complications arise when one or more of these boundaries become mobile on the timescale of diffusion—common examples include deformation (mobility of dislocations or subgrain boundaries) and reaction (mobility of mineral interfaces/surfaces). This is an area where little information (e.g., Yund & Tullis 1991) is available in the mineralogical literature in spite of its importance, and more research is required.

Figures 8 and 9a also illustrate how the energetically more demanding (higher activation energy) volume diffusion process dominates at higher temperatures over grain boundary and surface diffusion processes. That this behavior is not hypothetical is illustrated in **Figure 9b** using results of an experiment with an olivine bicrystal. These observations bring home a second crucial point about atomic transport—the efficiency of transport depends not only on the diffusion rate (i.e., magnitude of diffusion coefficient) but also on the availability of diffusion paths (e.g., concentration of point defects, steepness of concentration gradients, or solubility of elements/defects in the grain boundary region). That observable diffusive flux is the result of a combination

of diffusion coefficient and concentration gradient is the content of Fick's first law of diffusion (Equation 1, above) and is widely appreciated. That a combination of grain boundary solubility (number of atoms of a species actually found in a grain boundary) and grain boundary diffusion coefficient is analogously responsible for the ultimate efficiency of transport through a given grain boundary is equally significant but less commonly recognized (e.g., see Brady 1983, Baumgartner & Rumble 1988, Dohmen et al. 2003, Dohmen & Chakraborty 2003, Dohmen 2007).

In the course of a study on the nature of evaporation and condensation of olivines in the solar nebula, Dohmen et al. (1998, 2003) discovered that the surfaces of olivine crystals were not equilibrating with the surrounding medium instantaneously, even though the medium (a high temperature gas) was one in which transport rates were infinitely fast! A series of controlled experiments (Dohmen et al. 2003) and analysis



(Dohmen et al. 2003, Dohmen & Chakraborty 2003) revealed that element exchange in mineralogical systems can be classified into many more types than the conventional surface reaction control and diffusion control mechanism. It is necessary to understand the behavior adequately before the concentration gradients can be modeled to extract timescales. Dohmen & Chakraborty (2003) could identify at least six different kinds of reaction mechanisms (e.g., solid diffusion controlled, fluid diffusion controlled, surface reaction controlled, and various combinations of these, e.g., mixed solid diffusion and surface reaction controlled) and derive a reaction mechanism map (**Figure 10**). With the help of simple, measurable parameters it is possible to use this map to predict the expected reaction behavior in given systems. Some important observations in the current context are the following:

- (a) Coexistence of two homogeneous, mutually separated crystals need not mean that they are in equilibrium with each other, and the timescale of equilibration of such crystals may not always be given by simple $\sqrt{(Dt)}$.
- (b) In many cases, the single parameter γ/δ (see caption of **Figure 10** for notation) completely defines the reaction behavior of the system. Here the reaction



Figure 9

(a) Various modes of diffusion in a polycrystalline material and its continuum representation. Lattice/volume diffusion (vol) (*yellow paths*): diffusion in uninterrupted crystal lattice; subgrain diffusion (sGb) (*thin pink lines*): diffusion along subgrain boundaries within a mineral grain; grain boundary diffusion (Gb) (*thick pink lines*): diffusion along the boundary between two grains of the same mineral; intergranular diffusion (IGb) (also *thick pink lines*): diffusion along the boundary between two dissimilar grains; and surface diffusion (surf) (*green*): diffusion along the surface of the material. Activation energies, Q , may be expected to follow $Q_{vol} > Q_{Gb} \sim Q_{IGb} \sim Q_{sGb} > Q_{surf}$, and correspondingly, volume diffusion dominates at highest temperatures and coarse grain sizes—when the available paths for this mode of diffusion far outweigh the faster diffusion along discontinuities such as grain boundaries. For macroscopic modeling, it is possible to treat this entire material as one continuum, represented by a representative elemental volume (REV), shown here with the dashed line boundary. If the average concentration at the top of this region, C_2 , is higher than the average concentration at the bottom of the region, C_1 , (*shown in blue shades*) then a net flux of atoms (*thick blue arrows*) would occur from top to bottom. The proportionality constant that relates this flux to the concentration difference, $(C_2 - C_1)$, would be the diffusion coefficient, D , of the medium. Various constitutive law-type formalisms are available for relating the diffusion coefficients of the individual processes noted above (*fluxes for which are shown by thin arrows*) to D by using different weighted averaging schemes. (b) Experimental demonstration that grain boundary diffusion is not faster than volume diffusion at high temperatures. The sample consists of a bicrystal of synthetic forsterite with a single, well-defined (21° mismatch) grain boundary between them. This was surrounded by powdered fayalite and annealed under controlled oxygen fugacity at 1300°C for 72 h to induce diffusion. The elemental mapping (*warm colors*: higher Fe content) shows that diffusion through the lattice is faster and dominates the net exchange. The diffusion direction of Fe atoms is shown by a white arrow. The blue rim on the right is an artifact that results from scanning the epoxy in which the crystal (removed from the fayalite matrix that surrounded it during the experiment) is embedded. The thin green line on the right approximately corresponds to the surface of the forsterite bicrystal. There is no enhanced diffusion along the grain boundary at these conditions. This is consistent with results of calculations based on known rates of diffusion in olivine.

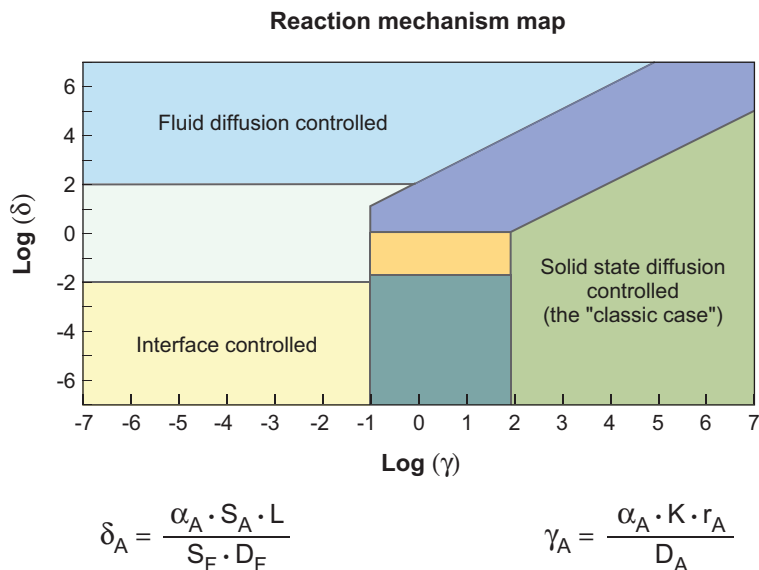


Figure 10

A reaction mechanism map for element/isotopic exchange between two physically separated crystals by diffusion mediated by an intergranular medium. The process is controlled by two dimensionless parameters, γ and δ , defined in the figure, where α is a surface reaction rate constant, K is a partition coefficient defined as (concentration in fluid)/(concentration in solid), r is the radius/characteristic width of the crystal participating in the exchange, D is the diffusion coefficient of the species in the crystal, s_A and s_F are the surface areas of the mineral and fluid, respectively, L is the length of the intergranular channel, and D_F is the diffusion coefficient in the fluid. As can be seen from the different-colored fields in the map, there are many possible reaction mechanisms, all of which can be predicted. The parameter γ/δ mainly controls the reaction mechanism of systems when $\delta > 1$, which eliminates the need to know the elusive parameter, α . If the ratio γ/δ is greater than 100 for a system, then the exchange is solid diffusion controlled and the resulting concentration profiles are more easily amenable to diffusion modeling for extracting timescales.

behavior becomes independent of the less accessible surface reaction kinetics rate and is defined by

$$\frac{\gamma_A}{\delta_A} = K i \cdot \frac{D_F \cdot S_F \cdot r_A}{D_A \cdot S_A \cdot L}$$

If the ratio γ/δ is greater than 100, the reaction will be solid diffusion controlled, whereas for $\gamma/\delta < 0.01$ it will be fluid diffusion controlled. Obviously, this value can be attained in a number of different, but for the reaction mechanism equivalent, ways. For example, increasing diffusivity in the fluid (e.g., an aqueous film as opposed to a dry grain boundary) will shift the reaction toward solid diffusion control, whereas if the surface area of the solid is large (e.g., small grain size), the reaction mechanism may shift back to fluid diffusion control.

In other words, these parameters allow the complex couplings to be evaluated using the reaction mechanism map.

- (c) One of the most significant findings of the analysis was the observation that the parameter K_i plays a very prominent role in controlling the reaction mechanism. The role of this “grain boundary solubility” has been discussed by Brady (1983) as well as Baumgartner & Rumble (1988), and more recently by Hiraga et al. (2004) and Hiraga & Kohlstedt (2007). The concept is well established in the materials science literature as the segregation factor, a quantity that plays a central role in material processing. This parameter is particularly important when considering the transport of an element through a grain boundary medium/fluid where its concentration is not particularly high (e.g., the transport of Fe and Mg atoms through a quartzofeldspathic matrix). As shown by the original experiments of Dohmen et al. (2003), fast transport rates alone do not ensure rapid equilibration; the medium needs to have the capacity to transport enough atoms of the species of interest as well. Dohmen et al. (2003) and Dohmen & Chakraborty (2003) demonstrated that if the grain boundary changes from one containing an aqueous fluid to a dry one, then (a) the closure temperature of a geothermometric system, e.g., Fe-Mg exchange between garnet and biotite, can differ by several hundreds of degrees; (b) the shape and width of the compositional profile will be very different; and (c) the timescale of equilibration will be dramatically different (e.g., several hundred thousand years versus several tens of millions of years), all other factors remaining the same. The role of K_i can explain many observations in natural systems, e.g., why equilibration rates, particularly of certain relatively insoluble trace elements, often drop dramatically once the solidus of a rock is crossed during cooling (in terms of the model system, the grain boundary fluid changes from a melt with high solubility of the element of interest to an aqueous fluid or a dry grain boundary).

The main use of the reaction mechanism map in measuring timescales lies in the fact that it allows suitable systems to be identified for modeling. Clearly, systems that reacted by the solid diffusion control mechanism are the most suitable for diffusion modeling. Dohmen & Chakraborty (2003) provide many criteria for inferring reaction mechanisms from observations of the reaction product and the nature of compositional zoning. One of the most useful criteria is to study the element concentration maps of crystals—if the composition at the rim of a crystal is the same at all places, irrespective of the phase in contact, then the reaction mechanism was most likely to have been solid diffusion control and grain boundary transport was efficient (which is not the same as saying it was merely fast). Such crystals are particularly suitable for diffusion modeling because grain boundary processes need not be considered explicitly and simple equilibrium boundary conditions suffice. Crystals that have reacted by other mechanisms can be used as well as long as the particulars of a specific reaction mechanism are adequately addressed; see Dohmen & Chakraborty (2003) for some sample calculations.

WHAT CONTROLS DIFFUSION IN SOLIDS?

Diffusive flux is determined by factors that control the concentration gradient as well as the diffusion coefficient (see Equation 1*a*). In any given diffusion problem the concentration gradient is controlled by the initial and boundary conditions, which in turn in any real system are determined by factors such as partition coefficients, texture, and modal abundance of minerals. Partition coefficients in turn depend on thermodynamic intensive variables, such as temperature, pressure, and fugacities of relevant species. The values of diffusion coefficients in common silicate systems are controlled by temperature, pressure, the state of strain/deformation, water fugacity, oxygen fugacity, composition, and anisotropy. Of these, temperature always has a strong effect; pressure and composition nominally always affect diffusion coefficients even if that effect may be undetectably small in many systems, and the remaining parameters may/may not influence diffusion in specific systems. In addition, different isotopes of a given element also diffuse at different rates, although the differences are small. However, sometimes this effect is detectable and can be put to use.

Temperature and pressure. The temperature and pressure dependence of diffusion coefficients can be combined to yield an Arrhenius-type equation that is obeyed at most conditions:

$$D(P, T) = D_0 \exp \left[\frac{-Q - \Delta V(P - 10^5)}{RT} \right], \quad (2)$$

where $D(P, T)$ is the diffusion coefficient at pressure P in Pascals, T is temperature in Kelvin, D_0 is termed the preexponential factor and represents diffusion coefficient at infinite temperature at atmospheric pressure, Q is the activation energy, ΔV the activation volume of diffusion, and R is the gas constant. The activation energy, Q (or activation volume, ΔV), can be interpreted in a number of different ways: (*a*) it is a measure of the reduction of diffusion rate due to a drop in temperature (or increase of pressure, if ΔV is positive); (*b*) it is a measure of the difficulty of diffusion; (*c*) the argument of the exponential factor is like a modulus, where the available thermal energy for diffusive jumps, RT , is compared to the energy barrier in the way of diffusive jumps, $[Q + \Delta V(P - 10^5)]$. Higher values of Q (or ΔV) imply slower diffusion at lower temperatures, but it also means that the process is more effective at higher temperatures. The aspect of difficulty, or energy barrier an atom/ion has to cross for diffusion to occur, is closely related to the activation energy barrier of chemical reactions in the context of the transition state theory, and exactly analogous formulations may be developed (e.g., see Allnatt & Lidiard 1993, which contains a summary of Lidiard's original works establishing these relationships). However, atomic transport in complex solids such as minerals rarely consists of a single elementary step of an atomic jump. More commonly, the macroscopic activation energy is the sum of several such microscopic jump processes and energies of formation of defects, etc. This is one reason why a compensation law is not necessarily expected to work in these systems. For example, it does not seem to work for divalent cations in olivine (Chakraborty 1997, Dohmen et al. 2007, Dohmen & Chakraborty 2007, Petry et al.

2004, and Coogan et al. 2005a), although for oxygen diffusion in minerals, it has been more successful, subject to certain restrictions (see Zheng & Fu 1998 and Cole & Chakraborty 2001 for reviews).

For divalent cations, activation energies tend to range between 200 [e.g., spinel (Liermann & Ganguly 2002), olivine (Dohmen & Chakraborty 2007)] and 300 [garnet (Ganguly et al. 1998), orthopyroxene (ter Heege et al. 2006)] kJ mol^{-1} . For trivalent cations, the activation energies lie between 340 and 250 kJ mol^{-1} (Van Orman et al. 2001, 2002; Tirone et al. 2005), and for Silicon, activation energies are on the order of 400–500 kJ mol^{-1} (Dohmen et al. 2002b, Costa & Chakraborty 2007). The highest activation energies in any silicates are found in zircon [840 kJ mol^{-1} for diffusion of Sm (Cherniak et al. 1997a)]. Oxygen diffusion can have a wide range of activation energies (see Cole & Chakraborty 2001 for details). The effect of pressure on diffusion rates in solids has been reviewed by Bejina et al. (2003). The activation volumes for diffusion in solid minerals have a positive sign and lie in magnitude between $(0 - 16) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. More recently, Holzapfel et al. (2007) have discussed the data reduction for high-pressure experiments and some of the potential pitfalls. One of their interesting findings is that within the Earth, diffusion rates increase with depth up to the bottom of the lithosphere, but the gentler asthenospheric geothermal gradient results in the pressure effect overwhelming the thermal effect and diffusion rates actually decrease with depth, even if the temperature increases. This makes the lithosphere-asthenosphere boundary a region of diffusion maximum or a region of enhanced mixing and other chemical processes.

Variety of diffusion coefficients. There are a variety of different kinds of diffusion coefficients that may be defined for mineralogical systems (e.g., self-diffusion coefficient, tracer diffusion coefficient, interdiffusion coefficient, chemical diffusion coefficient, multicomponent diffusion coefficient matrices, and effective binary diffusion coefficient), and all of these are, in principle, a function of composition. The review by Ganguly (2002) discusses these aspects in some detail.

Fluids. All of these diffusion coefficients may depend on fluid fugacities as well. We note here only briefly that for volume diffusion in crystals, this effect arises from the fluid fugacities influencing the concentration of point defects in the crystal in some manner; a detailed discussion of these aspects is beyond the scope of this article. Some examples of discussion of how fluids (mainly water) may affect point defects, and how these in turn may affect diffusion rates, may be found in Farver & Yund (1991), Hier-Majumder et al. (2005), and Costa & Chakraborty (2007).

Anisotropy. Diffusion coefficients in crystals are anisotropic in exactly the same manner as the optical properties (refractive indices) because both are physical properties that are described by tensors of rank two. Therefore, one can define a diffusion indicatrix just like the optical one and all considerations that apply to the optical properties also apply to anisotropy of diffusion. Diffusion along an arbitrary direction in

a crystal is given by

$$D = D_a(\cos \alpha)^2 + D_b(\cos \beta)^2 + D_c(\cos \gamma)^2,$$

where D_a , D_b , and D_c are the diffusion coefficients along the principal axes (which may or may not coincide with directions of symmetry axes depending on crystal class, just like an optical indicatrix) and α , β , and γ are the angles the direction of interest makes with these axes.

Isotope effect. With increasing resolution of modern mass spectrometers and the ability to study the isotopic fractionation of elements as heavy as Fe, the question of if and how isotopes fractionate during diffusion in solid minerals is becoming increasingly important. At the other extreme, with the increasing geochemical significance of light elements such as Li and B, isotopic effects on diffusion rates are turning out to be critical for evaluating geochemical data. Based on analysis in simple model systems, the dependence of diffusion coefficients on isotopic mass is expected to follow (e.g., see Bokhstein et al. 1985, Ganguly 2002)

$$\left(\frac{\Delta D}{D_{i(\beta)}^*} \right) \approx f_\alpha \left[\left(\frac{M_\beta}{M_\alpha} \right)^q - 1 \right],$$

where α and β are the two isotopes, ΔD is the difference in diffusion rate between the two isotopes, $D_{i(\beta)}^*$ is the tracer diffusion coefficient of isotope β , M_α , etc., is the mass of isotope α , f_α is an averaged dynamic correlation factor, and the parameter q carries information about the nature of the diffusive jump. The conventionally written value of $q = 0.5$ is only valid when the jumping atom contributes all the kinetic energy for that mode of motion. If accurate diffusion coefficients of different isotopes are available, then deviation of q from 0.5 can provide interesting insight into lattice dynamics, providing a bridge between mineral physics and geochemistry. Recent studies on Li diffusion in glasses and solids appear to be providing some information of this nature (Richter et al. 2003, 2006; Teng et al. 2006). Ability to determine diffusion coefficients at increasingly high pressures may make this an important tool for exploring lattice dynamics at conditions where direct measurements may be difficult.

Stress and deformation. Finally, a widely discussed and controversial topic is the role of stress in controlling diffusion. Space does not permit a detailed analysis of this controversial issue here, but I note that much of the controversy arises because the influence of stress on diffusion processes manifests through several different physical effects. Some significant points to note are the following:

- (a) The diffusion coefficient is like a thermodynamic quantity and therefore depends on the state of a material, but not on gradients. Therefore, it depends on nonisostatic stress at a point (where a point is defined in the spirit of a representative elemental volume, as discussed above) but not on gradient of stress.
- (b) The nature of the medium in which diffusion occurs is altered by stress. It is altered, for example, by a change in the concentration and distribution of planar

defects such as dislocations in response to a stress gradient. This is the plastic component of deformation. The driving force may be altered, for example, by raising/lowering the energy barrier (by addition/subtraction of an elastic strain energy term) that a diffusing atom has to cross for diffusion to occur. This is the elastic effect. In addition to occurring in parallel, these two responses to a stress gradient occur on different timescales—the plastic deformation is controlled by a finite velocity of dislocations whereas the elastic strain is propagated with the velocity of sound through a material, i.e., is instantaneous for most practical applications. This coupling of different phenomena that occur in response to one stimulus (a stress gradient) on different timescales is the cause for confusion in the handling of the effect of stress on diffusion. Compositional change may result from dislocations sweeping through a region of a solid undergoing plastic deformation, where these dislocations provide mobile shortcuts. This may be considered to be a special case of a stress gradient altering the state of a material in which diffusion occurs, and is likely to be one of the most important contributors to the enhancement of diffusive equilibration during deformation (e.g., see Yund & Tullis 1991).

- (c) The boundary conditions subject to which diffusion occurs may be altered by stress. The equilibrium concentrations of point defects at two different surfaces of a solid at different states of stress are different. And finally, application of a homogeneous stress field on a heterogeneous medium, or even a homogeneous medium with complex geometry (e.g., curved surfaces), may generate stress gradients.

All effects are possible, and indeed, typically occur simultaneously, resulting in the confusion in the description of the effect of stress on diffusion.

DIFFUSION MODELING AND TIMESCALES OF GEOLOGICAL AND PLANETARY PROCESSES

Having discussed the nature of diffusion in solid minerals and the factors that control it, I present below a selection of applications of diffusion modeling to extract timescales. The selection is intended to be representative of the variety of systems and timescales that can be studied and has been compiled with the aim of guiding future users to as wide a range of modeling techniques/tools as is possible within the limited available space. It is not a comprehensive listing of all applications of diffusion modeling to extract timescales.

Costa & Dungan (2005) exploited the full power of modern diffusion modeling to (a) model concentration gradients of several elements (Fe-Mg, Mn, Ni, Ca) in the same olivine crystals, (b) make use of diffusion anisotropy to obtain timescales from profiles of different lengths measured along different directions in the same crystal, and (c) carry out such measurements on multiple crystals in the same thin section to obtain robust estimates (up to 300 independent determinations!) of timescales of assimilation of gabbroic rocks in subduction zone volcanoes of only a few years to a decade. Such timescales are short enough to be within the realm of interest for human planning. The method can be applied with the same resolution to rocks and meteorites

of any age. In a related approach, Morgan & Blake (2006) make use of differences in diffusion rates between two elements in a mineral (Sr and Ba in plagioclase) to extract timescales of volcanic processes.

In another application of diffusion modeling to minerals (plagioclase in this case) from volcanic rocks, Costa et al. (2003) demonstrated that diffusion of trace elements may in fact be strongly coupled to distribution and diffusion of major elements and needs to be considered to obtain accurate results. Multicomponent modeling, accounting for full diffusive coupling, was used by Faryad & Chakraborty (2005) to determine that rapid exhumation (>4 cm year⁻¹) and cooling (~ 100 – $200^\circ\text{C Ma}^{-1}$) occurred at plate tectonic velocities in the eastern Alps during the Cretaceous. Simultaneous fitting of compositional profiles of multiple elements provides tighter constraints than the use of effective binary diffusion coefficients (EBDC) to fit one profile at a time (e.g., Ganguly et al. 1996). In a similar approach, Ague & Baxter (2007) used Sr zoning in apatite and major element zoning in garnet in combination to determine that the thermal pulse that led to the formation of the classic Barrovian metamorphic zone in Scotland lasted only approximately a few hundred thousand years. This kind of information shows that several short-lived pulsed episodes of metamorphism and fluid production combine to produce orogenic events that last tens of millions of years. All of the examples listed so far were benefited (i.e., were better constrained) by the use of diffusion rates of more than one element in a mineral in one way or another. In natural systems, diffusion occurs simultaneously with the processes of crystal growth or dissolution (a moving boundary problem). Although it is difficult to use compositional zoning in such crystals to extract information on timescales (unknown extent of and kinetic law governing growth/dissolution), Ganguly et al. (2001) could model the extent of crystal dissolution during the second stage corona-forming reaction in granulites from the Prydz Bay, Antarctica, to constrain the duration of the pan-African metamorphic event in the area to be between 5–15 million years. As rocks evolve along a temperature-time path, it is expected that boundary conditions that govern diffusion in a crystal (e.g., the size of the surrounding equilibrating volume) would change. Hauenberger et al. (2005) studied diffusion profiles in garnets coexisting with biotite in granulites from the Neoproterozoic Mozambique belt in SE Kenya, paying careful attention to the details of the zoning profile. They found that the volume with which the garnet was in element exchange equilibrium decreased sharply at approximately the solidus temperatures of the concerned rocks. Such a change in the size of the equilibrating volume with temperature is consistent with the predictions of the element exchange model of Dohmen & Chakraborty (2003) because the mean solubility of rock-forming elements in the grain boundary region would be very different in a melt present versus a dry system. The modeling of Hauenberger et al. (2005), considering such variations as a function of time, yielded a nonlinear cooling history, of which the first part matched exactly with independently constrained cooling rate from isotopic dating (e.g., Nd isotopes). Similarly, Ganguly et al. (2000) modeled zoning profiles in garnets from the Sikkim Himalaya to also obtain a two-stage history. But in addition, they combined the thermal history to a pressure-temperature path to obtain a two-stage exhumation history—a rapid exhumation at 15 mm year⁻¹ to midcrustal depths of approximately 15 km, followed by

much slower exhumation at $\sim 2 \text{ mm year}^{-1}$ to shallower depths. A second interesting aspect of the paper is the demonstration of how sectioning effects (thin section cuts not going through exact centers of crystals) can result in incorrect cooling histories. A simple recipe is provided in the paper to avoid this common pitfall. Other similar pitfalls include effects arising from sections inclined at an angle to the diffusion interface and from concentrations in the plane of observation being modified by diffusion in the unknown third dimension, the latter particularly important for crystals in which diffusion is anisotropic (e.g., olivine).

We discussed above the advantages of using the full zoning profile for the determination of timescales, and this remains by far the preferred tool where enough observational and diffusion data are available. In the absence of this full body of information, however, alternate approaches can nevertheless yield first-order information on timescales, albeit with more assumptions (e.g., about concentration profile shapes) and uncertainties. I describe here two methods of this kind that have been suggested in the literature.

All of the processes that we have been discussing may occur in extraterrestrial samples as well, and, indeed, there is a rich literature on calculation of cooling rates and other aspects of thermal history in the meteoritic literature. In particular, in recent years Ganguly and coworkers have made many successful applications and new developments of diffusion modeling to infer timescales. I discuss the work by Ganguly & Tirone (2001) as one that addressed some major issues, using one such approximate method. They used two developments in modeling technique from their own work to study a suite of H-chondrites and mesosiderites. These methodological developments were (a) the use of the difference between ages obtained from core and rim compositions to obtain cooling rates, and (b) the extension of the Dodson formulation for relatively slowly diffusing species that retain memories of their initial conditions, as discussed above. The results not only showed that there was a systematic correlation between metamorphic grade and cooling history but also that there was excellent consistency between their results (for higher temperature parts of the histories) and metallographic cooling rates (also based on diffusion modeling, but relevant for lower temperature parts of the histories). But most significantly, they resolved a long-lasting dilemma about the somewhat younger age of the Morristown mesosiderite based on a Sm-Nd mineral isochron (approximately 90 million years younger than that based on Pb-Pb ages of other mesosiderites). Their improved analysis of diffusion during cooling showed that the younger age was likely the result of resetting during cooling and thus instead of being a dilemma or being related to unqualified thermal spikes, the younger age actually places constraints on the cooling histories of these mesosiderites.

Jaoul & Bejina (2005) suggest a method that draws on the validity of compensation law in addition to the uncertainties about profile shapes. They demonstrate that the method works for estimating cooling rates from oxygen isotopic diffusion profiles in coexisting diopside and calcites from marbles in the Adirondack highlands. The approach makes use of the fact that if a distribution of grain size is available and it can be demonstrated/assumed that the concentration gradients arise entirely from diffusive exchange, then the average compositions of grains of different sizes may

be used to estimate the activation energy of diffusion. Next, if a compensation law is valid, then it may be used to determine the preexponential factor, and using this diffusion coefficient, the cooling rate can be estimated. Clearly, the method relies on several assumptions but is likely to be particularly valuable where no experimentally measured diffusion coefficients are available and a compensation law is valid. For reasons discussed above, the compensation law is more likely to be valid for oxygen diffusion in silicates of a specific type, and it is in the modeling of oxygen isotopic distributions that the method is likely to find its most successful applications.

Although many of these applications are in high-temperature igneous and metamorphic systems, the ability to measure concentration profiles of an increasing variety of species is rapidly expanding the range of processes that can be studied using these tools. One particularly interesting example is the study of Li diffusion, which appears to be unusually fast in at least some silicates (e.g., plagioclase, diopside). Coogan et al. (2005b) studied Li diffusion profiles in plagioclase—pyroxene pairs from oceanic lavas and dikes to map the cooling history as a function of depth in a section of the oceanic crust (Costa Rica rift, ODP Hole 504B). Their finding of strong variation of cooling rate with depth allowed them to constrain the transient change in permeability of the oceanic crust during emplacement of dikes of the sheeted dike complex. Moreover, the calculated energy liberated from the cooling of such dikes was found to be sufficient to power the formation of oceanic hydrothermal megaplumes, allowing them to couple high-temperature igneous processes (cooling of dikes) with low-temperature oceanographic phenomenon ($<1^{\circ}\text{C}$ temperature anomalies in the water column).

Finally, Demouchy et al. (2006) and Peslier & Luhr (2006) used diffusion rates of water in olivines to determine extremely rapid rates of magma ascent from the mantle. According to these results, magma traveled several tens of kilometers in a few hours to days (less than a week). Such modeling is unlikely to yield correct results if anisotropy and different mechanisms of water diffusion are not properly accounted for, and if suitable boundary conditions are not imposed in the modeling. However, enough information is available now to allow these details to be considered and to retrieve timescales of such extremely rapid geological processes.

In summary, we find that diffusion modeling can help us identify processes occurring on a variety of timescales, from days and decades to millions of years, irrespective of the age of the record. The robust quantification that is now becoming possible is an important step toward understanding how the hierarchical timescales of high- as well as low-temperature processes link together like the different sized gears in clockwork to produce the dynamic system that is planet Earth.

SUMMARY POINTS

1. Diffusion in the solid state is a widespread process that has many attributes that allow it to function as a clock for measuring durations of a variety of terrestrial and planetary processes.

2. The diffusion clock can measure the duration of very short (days) as well as long (millions of years) processes, and its functioning is independent of the age of the material. This makes it particularly valuable for studying short processes in the early history of Earth and the Solar System.
3. Uncertainties in measurements of diffusion coefficients and their extrapolations to model natural systems made the tool only of limited use in the past. Recent technological advances that allow manipulation (experiments, chemical analysis, and structural characterization) of materials on the nanoscale are removing many of these shortcomings. Notably, for many applications in modeling studies, it is now possible to interpolate, rather than extrapolate, diffusion coefficients measured in the laboratory.
4. Our understanding of point defects and diffusion mechanisms in realistic natural mineral compositions is improving rapidly so that it is possible to critically evaluate diffusion data before using them to model processes.
5. Diffusion modeling is revealing a wide hierarchy of timescales, ranging from days to millions of years, and is thereby providing considerable insight into dynamic processes and the nature of their coupling. For example, it is now possible to dissect orogenies or volcanic eruptions to study the individual thermal pulses that cause them; a variety of other applications are possible and some have been outlined here.

FUTURE DIRECTIONS

1. A new view of timescales: By far the most significant impact will result from the diversity of timescales of processes that are becoming accessible and are being unraveled. This is fundamentally altering our view of the role of time in the Earth sciences, and the fallout of such insights is likely to be broad and unpredictable. Studying how short pulses add up to make mountains out of molehills will occupy Earth scientists in the days to come.
2. Other applications of diffusion data and modeling: Although not covered in this review, the increased abundance and quality of diffusion data will help progress in a variety of other areas, such as rheology of Earth materials or mechanisms of mineral reactions.
3. Determination of diffusion coefficients: With the new experimental tools that are just becoming available (thin film technology, analytical tools such as Nanosims, field emission electron microprobes, and ATEM), determination of more accurate diffusion coefficients for a wide range of elements in a wider range of minerals will be possible. The conditions at which such measurements can be made will also be substantially expanded (e.g., miniaturization will allow pressures attainable only by diamond anvil cells to be

accessed). Measurements carried out in defective crystals [e.g., radiation damaged crystals (Cherniak & Watson 2003)] and in crystals with mobile defects (owing to deformation, chemical reaction) will be the next challenge for experimental measurements. Diffusion measurements in polycrystalline materials will expand enormously in the days to come. These measurements should be anchored firmly by analysis of point defect thermodynamics when possible.

4. Computational models: Ab initio calculations of defect states and migration in realistic iron-bearing systems will contribute significantly to our understanding of diffusion behavior. On a different scale, models of reaction with diffusion and other moving boundary problems solved numerically will considerably expand the scope of diffusion modeling. Almost all diffusion modeling to obtain timescales will be numerical, moving away from the older “geospeedometric” formulations. Formulations for multipath diffusion and other schemes of obtaining averages for representative elemental volume will multiply as more data becomes available.
5. Analytical advance: Concentration profiles of an increasing number of species will be measured with increasingly high spatial resolution, providing much more material for diffusion modeling as well as for constraining the models. The samples being modeled will be better characterized structurally as well.
6. Theory of diffusion processes: As illustrated through simple examples in the text, much of our understanding of diffusion in solids stems from data on simple materials, such as metals, and from diffusion studied under relatively “benign” conditions. Complex silicates placed in extremes of environments (pressure, temperature, strain rates) demand a much broader theoretical apparatus that includes addressing the effects of diffusive coupling, defect clustering, interaction between diffusion and various linear and planar defects, and the complex roles of stress and fluids, to name a few. Feedback between these and newer measurements will considerably enhance our understanding of diffusive processes, leading to more sophisticated models to extract timescales with lesser uncertainties.

DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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